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(54) **Coated activated carbon**

(57) A process is disclosed for application of a polymer coating on a granular or shaped activated carbon to essentially eliminate or to significantly reduce product attrition by dusting without a reduction in adsorption ve-

locity or capacity of the activated carbon. After the polymer coating has dried, any residual carbon dust is removed. New products resulting from the disclosed process also are disclosed.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to activated carbon pellets and activated granules with improved dusting characteristics. In particular, this invention relates to activated carbons susceptible to dust attrition due to abrasion where dusting can result in loss of product and often cause other problems related to product end-use.

Description of Related Art

[0002] Active carbon long has been used for removal of impurities and recovery of useful substances from liquids and gases because of its high adsorptive capacity. Generally, "activation" refers to any of the various processes by which the pore structure is enhanced. Typical commercial activated carbon products exhibit a surface area (as measured by nitrogen adsorption as used in the B.E.T. model) of at least 300 m²/g. For the purposes of this disclosure, the terms "active carbon" and "activated carbon" are used interchangeably. Typical activation processes involve treatment of carbon sources such as resin wastes, coal, coal coke, petroleum coke, lignites, polymeric materials, and lignocellulosic materials including pulp and paper, residues from pulp production, wood (like wood chips, sawdust, and wood flour), nut shell (like almond shell and coconut shell), kernel, and fruit pits (like olive and cherry stones) either thermally (with an oxidizing gas) or chemically (usually with phosphoric acid or metal salts, such as zinc chloride).

[0003] Chemical activation of wood-based carbon with phosphoric acid (H₃PO₄) is disclosed in U.S. Patent No. Re. 31,093 to improve the carbon's decolorizing and gas adsorbing abilities. Also, U.S. 5,162,286 teaches phosphoric acid activation of wood-based material which is particularly dense and which contains a relatively high (30%) lignin content, such as nut shell, fruit stone, and kernel. Phosphoric acid activation of lignocellulose material also is taught in U.S. 5,204,310 as a step in preparing carbons of high activity and high density.

[0004] Also, U.S. 4,769,359 teaches producing active carbon by treating coal cokes and chars, brown coals or lignites with a mixture of NaOH and KOH and heating to at least 500°C in an inert atmosphere. U.S. 5,102,855 discloses making high surface area activated carbon by treating newspapers and cotton linters with phosphoric acid or ammonium phosphate. Coal-type pitch is used as a precursor to prepare active carbon by treating with NaOH and/or KOH in U.S. 5,143,889.

[0005] Once the activated carbon product is prepared, however, it may be subject to some degradation before and during its use. Abrading during materials handling and actual use of such activated carbon results in loss of material in the form of dust. Such "dusting" of the product is a function of its relative hardness and its shape, as well as how it is handled in the plant in moving it into and out of plant inventory, in loading for transport and in off-loading by the receiver, and how it is handled by the receiver to place the product into use. In certain applications, such as employment in canisters in automobiles where the activated carbon is subject to constant vibration and may have to withstand collision, product degradation by dusting continues through the life of the product.

[0006] The hardness of an activated carbon material is primarily a function of the hardness of the precursor material, such as a typical coal-based activated carbon being harder than a typical wood-based activated carbon. The shape of granular activated carbon also is a function of the shape of the precursor material. The irregularity of shape of granular activated carbon, i.e., the availability of multiple sharp edges and corners, contributes to the dusting problem. Of course, relative hardness and shape of the activated carbon are both subject to modification. For example, U.S. Patent Nos. 4,677,086, 5,324,703, and 5,538,932 teach methods for making pelleted products of high density from lignocellulosic precursors. Also, U.S. Patent No. 5,039,651 teaches a method of producing shaped activated carbon from cellulosic and starch precursors in the form of "tablets, plates, pellets, briquettes, or the like." Further, U.S. Patent No. 4,221,695 discloses making an "Adsorbent for Artificial Organs" in the form of beads by mixing and dissolving petroleum pitch with an aromatic compound and a polymer or copolymer of a chain hydrocarbon, dispersing the resultant mixture in water giving rise to beads, and subjecting these beads to a series of treatments of removing of the aromatic hydrocarbon, infusibilizing, carbonizing, and finally activating.

[0007] Despite these and other methods of affecting activated carbon hardness and shape, however, product dusting continues to be a problem in certain applications. For example, in U.S. Patent No. 4,221,695, noted above, the patentees describe conventional beads of a petroleum pitch-based activated carbon intended for use as the adsorbent in artificial organs through which the blood is directly infused that are not perfectly free from carbon dust. They observe that some dust steals its way into the materials in the course of the preparation of the activated carbon, and some dust forms when molded beads are subjected to washing and other treatments. The patentees note that the application of a film-forming substance to the surface of the adsorbent "is nothing to be desired," because the applied substance acts to reduce the adsorption velocity of the matters to be adsorbed on the adsorbent and limit the molecular size of

such matters being adsorbed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a graphical representation of the butane working capacity (BWC) values of polymer coated, shaped activated carbons of various sources, as well as the effect of the polymer coating on their respective BWC values, as reported in Table III.

[0009] Figure 2 is a graphical representation of the initial dust values of polymer coated, shaped activated carbons of various sources, as well as the effect of the polymer coating on their respective initial dust values, as reported in Table III.

[0010] Figure 3 is a graphical representation of the dust rate values of polymer coated, shaped activated carbons of various sources, as well as the effect of the polymer coating on their respective dust rate values, as reported in Table III.

SUMMARY OF THE INVENTION

[0011] It has been discovered that product attrition by dusting of granular and shaped activated carbons can, in fact, be reduced significantly, or essentially eliminated, by the application of a thin, continuous polymer coating on the granular or shaped activated carbon, without a reduction in adsorption velocity or capacity of the activated carbon. After the applied polymer coating has dried, any residual carbon dust is removed. The polymer coated granular or shaped activated carbon product exhibits a butane activity greater than 15 g/100g. Preferably, the polymer-coated granular or shaped activated carbon also exhibits a butane working capacity greater than 9.0 g/dL.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0012] In particular, dusty automotive carbon pellets pose potential problems in materials handling and in canister applications. A method is disclosed based on applying a visible polymer coating on the finished product and then removing any residual dust. The product is considered dust free, as shown by an "initial dust" value of ≤ 0.3 mg/dL and a "dust rate" value of ≤ 0.01 mg/min/dL, both below the detection limits of the standard dust attrition test. The product is "essentially" dust free, as shown by a "dust rate" value of ≤ 0.06 mg/min/dL, a detectable value but dramatically lower than the dust rate of uncoated activated carbon and, as noted in the Tables which follow in the Examples, is the highest dust rate value of the invention-treated activated carbons. Though both surprising and unexpected based on the prior art teaching noted above, the retention of butane adsorption and working capacity properties are an important feature of the coated pellets. As shown in the examples below, the coated pellets retained 94-100% of the uncoated pellet butane activity and 88-100% of the uncoated pellet butane working capacity (BWC). For example, the invention coated shaped and granular activated carbon will have a butane activity of greater than 15 g/100g, preferably greater than 25 g/100g, more preferably greater than 35 g/100g, even more preferably greater than 45 g/100g, even more preferably greater than 55 g/100g, even more preferably greater than 65 g/100g, and most preferably greater than 75 g/100g. Also, the invention coated shaped and granular activated carbon will have a butane working capacity greater than 9.0 g/dL, preferably greater than 10.0 g/dL, more preferably greater than 11.0 g/dL, even more preferably greater than 12.0 g/dL, even more preferably greater than 13.0 g/dL, even more preferably greater than 14.0 g/dL, and most preferably greater than 15.0 g/dL.

[0013] An additional feature is that this coating provides the pellets with a glossy and attractive appearance that calls attention to product cleanliness. The glossy nature of the coating results from the film-forming nature of the polymer and the emulsion form by which it is applied to the pellets. An added facility, and possible benefit, provided by the invention composition and process is achieved by the natural color of the coating material or by the addition of coloring agents, such as pigments and optical brighteners, to the polymer emulsion. In particular, distinct carbon products may be identified through color-coding. The color-coding may relate to product application, plant origination, customer designation, or any designation desired.

[0014] The coated shaped and granular activated carbon is also hydrophobic, as demonstrated by floating on water rather than rapidly wetting and sinking. In experiments with coated activated carbon pellets, half of the uncoated pellets sank in 26 seconds when placed in water, whereas the coated pellets were not penetrated by the water and floated for more than 6 days. The resistance to wetting and pore filling with liquid water may be of particular utility for vapor adsorber units in some bulk hydrocarbon storage applications. In those applications, the adsorbers are occasionally flooded with water to quench hot spots, but the adsorbers tend to be difficult to return to service due to water retained within the carbon porosity. Another potential use of the coated shaped or granular activated carbon is for the removal of trace organic compounds from water, where limiting the concentration of water in the pellet would increase the selectivity for the adsorption of the organic compounds. The coating could be tailored to be more permeable for the trace organic compound to be adsorbed and less permeable to the majority component, improving the adsorptive

capacity of the activated carbon.

[0015] The difference in appearance between the invention emulsion coated glossy pellets and previous dispersion-coated pellets is due to the different forms of the polymers used in applying the coatings. The particle sizes of emulsions are smaller than dispersions, therefore emulsions form continuous films due to the effects of capillary forces when dried of the carrier liquid. Dispersions do not form continuous films by drying, and they leave behind discrete (i.e., noncontinuous) polymer particles similar in size to the originally dispersed particles. The continuous, emulsion-applied polymer film, on the other hand, provides a glossy appearance, coating integrity, pellet dust reduction, and hydrophobicity that a dispersion-applied, non-continuous film does not.

[0016] Also, it should be noted that while the polymer film resulting from the application of the polymer emulsion onto the shaped or granular carbon is a continuous film, it may be porous or non-porous, depending on the irregularity of surface shape of the carbon material. The appearance of a porous continuous film occurs more often on the more irregular shaped granular activated carbons than on shaped activated carbons.

[0017] The process of the invention may be described as a process for essentially eliminating dust attrition of activated carbon material by coating the activated carbon material comprising the steps of:

(a) spraying an emulsion of the polymer onto exposed surfaces of the activated

carbon material while it is in a state of turbulence at a processing temperature above ambient temperature; and

(b) drying the coated activated carbon material at above ambient temperature.

The process may optionally include an initial step of preheating the active carbon material to above ambient temperature. Also, the process of the claimed invention may comprise a further step

(c) de-dusting the dry coated activated carbon material by removing any residual dust therefrom.

[0018] As those skilled in the art appreciate, various processing conditions are generally interdependent, such as processing time and processing temperature. These operating conditions as well may depend on the nature of the carbon material to be coated (shaped or granular, coal-based or lignocellulosic-based, etc.) and the coating material (relative volatility, viscosity, etc.). Thus, the temperature range for coating application and coating drying steps may range from ambient up to about 280°F (138°C), and the processing time may take from about 5 minutes to about 12 hours. For most combinations of shaped or granular active carbon material and coating material, a preferred operating temperature range for the coating and drying steps is from about 175°F (80°C) to about 250°F (121°C) for from about 30 minutes to about 6 hours.

[0019] The turbulent state of the active carbon material can be induced by various known means. For example, the carbon material, in granular or shaped (usually pellet) form, may be placed in a rotary tumbler, in a mixing device, or on a fluidized bed. While it is critical that the active carbon material be in a kinetic, rather than static, state when the coating material is applied to assure relative even coating on the surface area of the active carbon material, it is not critical how the kinetic state is achieved.

[0020] The product of the invention process may be described as a composition of matter comprising an activated carbon material exhibiting initial, pre-coating butane activity and butane working capacity values and having its surface coated with a continuous film of a polymer, said polymer film being operable for essentially eliminating attrition of the activated carbon material resulting from dusting and wherein the coated activated carbon material exhibits final, post-coating butane activity and butane working capacity values of 90-100% of the initial, pre-coating butane working capacity values, respectively.

[0021] The coating materials useful in the claimed invention are those capable of forming a continuous film. In particular, polymers, copolymers, and polymer blends that are suitable coating materials include: polyolefins, such as polyethylene, polypropylene, polyisobutylene, polystyrene, polyisoprene, polychloroprene, poly-4-methyl-1-pentene, polybutadiene, and polybutene; polyacrylics, such as polyacrylates, polymethyl methacrylate, polybutylmethacrylate, polymethacrylates, and polyacrylic acid; halogen-substituted alkanes, such as polytetrafluoroethylene, trifluoroethylene, vinyl fluoride, fluorovinylidene, fluorobutylene, and fluoropropylene; and other polymers including polyurethane, polyethylene terephthalate, styrene butadiene, modified polybutadiene, epoxies, modified alkyds, polyesters, starches, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, polyvinyl acetate, cellulose acetate, cellulose nitrate, cellulose triacetate, cellulose acetate, phthalate, cellulose propionate morpholinobutyrate, hydroxypropylmethyl cellulose, ethylene vinyl acetate, acrylic copolymers, polysulfones, polyether sulfones, polyethers, polyethylene, glycols, polyimines, polybutylene, polyvinyl ethers, polyvinyl esters, polyalkylsulfides, polyarylsulfides, ethers, polyvinyl esters, polyalkylsulfides, polyarylsulfides, lignosulfonates, polyacrylamide, cyanoacrylate, polyamides, polyimides, polysiloxanes, methacrylonitrile, polyacrylonitrile, polyvinyl pyridine, polyvinyl benzene, polyvinyl acetate, polyvinyl pyrrolidene, polyvinyl butyral, polyvinyl alcohol, polyvinyl chloride, polyvinyl formaldehyde, polyformaldehyde, polycarbonates, and

polyvinylidene chloride.

[0022] The shaped or granular active carbon material of the invention described herein may be derived from any known active carbon precursors including coal, lignocellulosic materials, including pulp and paper, residues from pulp production, wood (like wood chips, sawdust, and wood flour), nut shell (like almond shell and coconut shell), kernel, and fruit pits (like olive and cherry stones), petroleum, bone, and blood.

[0023] The following examples describe the method and properties of materials that have been treated according to the invention process.

Example 1

[0024] Two types of coatings were applied to pellets of Westvaco Corporation BAX 1100 activated carbon that provided dust free carbons: a high-density polyethylene (ChemCor polyethylene emulsion Poly Emulsion 325N35) and animoethylaminopropylpolysiloxane (General Electric silicone emulsion SM2059). Other polymers, including polypropylene and polystyrene, may be employed as alternative coating materials. Coating properties, such as abrasion resistance, permeability, and porosity, may also be further enhanced for a particular weight, density, particle size, and/or degree of cross-linking.

[0025] The activated carbon pellets were coated by tumbling in a rotating cylinder and initially heated to 250°F (121°C) using a hot air gun. An emulsion of the polymer was then sprayed on the carbon in successive doses as the activated carbon was maintained at about 150°F (66°C) under the hot air flow. (The emulsion of the polyethylene solution was 3.5 wt% solids. The emulsion of the polysiloxane solution was 3.9 wt% solids.) The coated activated carbon was then dried overnight at 220°F (105°C). After drying, any residual dust on the pellet exterior was removed by applying the vibration and airflow treatment of the first 10-20 minutes of the dust attrition test (described below). The final coated product has a shiny, smooth appearance, compared with the dull exterior of the uncoated material.

[0026] Table I compares the dust attrition, and butane properties for the uncoated and coated pellets. Data for a baseline sample using only de-ionized water for the spray are also included to prove the importance of the polymer coating on the change in dust properties. Dust attrition rates were measured with the two-point method in a 30-minute test (described below).

Table I

Sample ID	Coating Loading (wt%)	Initial Dust (mg/dL)	Dust Rate (mg/min/dL)	AD (g/mL)	Butane Activity (g/100g)	Butane Activity (g/dL)	BWC BWC	Butane Ratio
Uncoated ¹		11.4	0.69	0.361	35.0	12.6	10.9	0.864
				0.353	35.0	12.4	10.9	0.883
		11.4	0.69	0.357	35.0	12.5	10.9	0.874
Polyethylene Emulsion								
Run 1A	2.9 ²	0.00	0.00	0.361	33.0	11.9	102	0.858
Run 1B	1.6 ³	0.00	0.00	0.356	33.7	12.0	103	0.860
Silicone Emulsion								
Run 2	3.4 ⁴	0.00	0.00	0.349	32.3	11.3	9.6	0.854

¹ Same sample, duplicate measurements to obtain representative average reading.

² Derived as average of wet-basis weight gain (1.0 wt%) and emulsion weight used (4.8 wt%).

³ Derived as average of wet-basis weight gain (0.5 wt%) and emulsion weight used (2.8 wt%).

⁴ Derived as average of wet-basis weight gain (0.9 wt%) and emulsion weight used (5.8 wt%).

[0027] Initial dust and dust rate values were measured by a modified, 3-filter version of the "Standard Test Method for Dusting Attrition of Granular Carbon" (ASTM D5159-91). A 1.0 dL sample of carbon is placed on a screen with 0.250 mm openings in a test cell holder and is subjected to vibration of 40 m/s/s RMS acceleration and downward air flow of 7 L/min for a 10 minute interval. A glass fiber filter, placed below the sample screen, collects dust from the sample. The vibration and airflow step is conducted three times with three different filters. The dust rate is calculated by the following equation:

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$$\text{Dust Rate (mg/min/dL), DR} = 0.0732 w_3$$

where w_3 is the milligram weight gain of the third filter.

[0028] The dust rate from this equation is within a standard deviation of $\pm 13\%$ of the dust rate obtained by the standard ASTM procedure that uses filter weight data from three additional 10 minute test intervals.

[0029] The initial dust is calculated as the milligram weight gain for the first filter, w_1 , minus the amount of dust attrited within 10 minutes ($10 \times \text{DR}$):

$$\text{Initial Dust (mg/dL)} = w_1 - 10 \text{ DR.}$$

Note that the weight gain of the second filter, w_2 , is not directly applied in these calculations. However, the w_2 value has utility in confirming whether dust rate detection limits have been reached for a sample by showing a zero or negative weight gain.

[0030] The inherent error in dust rate is ± 0.01 mg/dL by a partial differential error analysis of its equation for calculation and the 0.1 mg readability of the four decimal place gram balance required in the procedure. Likewise, the inherent error in initial dust is ± 0.3 mg/dL. Therefore, the non-detect dust rate value would be 0.01 mg/min/dL and the initial dust value would be 0.3 mg/dL.

[0031] Compared with the reduction of initial dust, the sharp reduction in dust rate is the more important feature of the invention coated shaped or granular activated carbon materials. By definition, a dust rate of 0.01 mg/min/dL or less means that initial dust was removed within the attrition test to the detection limits of the test, and demonstrates that initial dust would be likewise readily removed by other means. Alternatively, complete removal of initial dust without a sharp reduction in dust rate is perceived as being comparatively less useful since dust would be expected to readily reappear upon exposure of the sample to inter-particle motion from vibration, agitation or other motive force acting thereon.

[0032] The butane activity and butane working capacity (BWC) values were determined according to the procedure disclosed in U.S. Patent No. 5,204,310 and such teaching is incorporated by reference herein.

[0033] The data in Example 1 show that, as a result of the polymer coatings, the treated samples show initial dust and dust rate values in the non-detect range.

Example 2

[0034] Further tests show that similarly coated activated carbon pellets (Westvaco Corporation BAX 1500) exhibit increased abrasion resistance, as measured by a standard pellet hardness test (CTC Procedure 960-130), which is a modified version of ASTM D3802-79 (ball pan hardness). The pellet hardness test involves shaking the sample (2 mm extruded carbon pellets) in a Ro-Tap Sieve Shaking Machine with stainless steel balls (10 of $\frac{3}{4}$ inch diameter and 20 of $\frac{1}{2}$ inch diameter) and measuring the amount of pellet breakage in terms of the change in mean particle size of particles collected in a special pan at the bottom of an equivalent 6 (full height) high sieve nest (consisting of #6, #8, #10, #12, #14, #18, and #60). Step 1: a standard sieve analysis is performed on 100 grams of sample material and the fractions of material on each sieve is weighed. Step 2: then the fractions are combined in the special pan with the 30 steel balls, and the special pan is shaken on the Ro-Tap for 20 minutes, after which the shaken sample is poured onto the top sieve of the sieve nest. Repeat steps 1 and 2, except the Ro-Tap time for step 2 is 10 minutes. Calculate the average particle size. The strength values are determined by dividing the mean particle diameter after grinding by the initial mean particle diameter and multiplying the quotient by 100.

[0035] One invention-prepared sample ("Run 3A") was as a composite of 10 replicate preparations using the polymer application method of Example 1. Another invention-prepared sample ("Run 3B") was prepared differently. A larger, 2-ft diameter rotating cylinder with lifters was used, and the samples was initially heated by indirect- and direct-fired burners rather than direct hot air flow. No de-dusting step was applied.

[0036] Table II compares the hardness, butane and dust attrition properties for the uncoated and coated pellets. Dust data were measured by a three-filter test method.

Table II

Sample ID	Coating Loading (wt%)	Pellet Hardness	AD (g/mL)	Butane Activity (g/100g)	Butane Activity (g/dL)	BWC (g/dL)	Butane Ratio	Initial Dust (mg/dL)	Dust Rate (nig/min/dL)
Uncoated	-	68.6	0.295	60.2	17.7	15.4	0.870	32	0.22
Coated									
Run 3A ¹	3.3	99.9	0.304	60.0	18.2	15.5	0.849	0.9	0.01
Run 3B ²	2.6	100.0	0.298	59.7	17.8	15.3	0.860	1.8	0.03

¹ Composite sample: Butane ratio, activity and BWC are average values for its 10 constituent replicate samples.

² Different preparation method vs. Run 3A, plus no de-dusting step employed to remove initial dust

[0037] The demonstration of increased hardness was made with 2 mm diameter BAX 1500 pellets of 68.6 hardness before coating. Pellets coated with about 1-3 wt% polyethylene have hardnesses of 99.9-100.0, indicating no change in mean particle size in the test. Compared with the uncoated pellets, the coated pellets retained 97-100% of the butane working capacity.

Example 3

[0038] To show that the invention process of dust attrition reduction or elimination is applicable to a variety of commercial activated carbons, samples of a shaped commercial coal-based activated carbon (Kuraray 3GX) and a shaped commercial olive pit-based activated carbon pellets (Norit CNR 115) were coated with polyethylene (9.0 wt% emulsion solids) and compared with a similarly coated shaped commercial wood-based activated carbon (Westvaco Corporation BAX 1500). The polymer coating has the same benefits as previously shown with wood-based BAX 1100 and BAX 1500 pellets for reducing dust without significant effect on key properties.

[0039] The coatings were applied by the previously described method of Example 1. A de-dusting step was not applied prior to analyses. The polymer loadings (coating wt.%) were determined by heating samples to 932°F (500°C) and measuring the amount of volatilized components with a hydrocarbon analyzer calibrated with carbons of known polyethylene content.

[0040] The results are shown in Table III and Figures 1, 2, and 3.

Table III

Sample ID	Measured Loading (wt%)	AD (g/mL)	Butane Activity (%)	Butane Activity (g/dL)	BWC (g/dL)	Butane Ratio	Initial Dust (mg/dL)	Dust Rate (mg/min/dL)
2 mm wood-based								
Uncoated*								
	--	0.282	66.5	18.8	16.2	0.865	2.24	0.15
	--	0.283	62.9	17.8	15.8	0.890	3.31	0.11
average:		0.283	64.7	18.3	16.0	0.878	2.78	0.13
Coated								
Run 4A	0.4	0.279	65.1	18.2	15.7	0.863	1.42	0.06
Run 4B	1.1	0.282	65.1	18.4	16.0	0.868	0.81	0.03
Run 4C	2.4	0.288	63.8	18.4	15.9	0.867	0.28	0.02

* Same sample, duplicate measurements--to obtain representative average reading.

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Table III (continued)

Sample ID	Measured Loading (wt%)	AD (g/mL)	Butane Activity (%)	Butane Activity (g/dL)	BWC (g/dL)	Butane Ratio	Initial Dust (mg/dL)	Dust Rate (mg/min/dL)
2.8 mm coal-based								
Uncoated*								
	--	0.326	51.3	16.7	14.4	0.859		
	--	0.323	50.7	16.4	14.2	0.870	6.76	0.53
average:		0.325	51.0	16.6	14.3	0.864	6.76	0.53
Coated								
Run 5A	0.7	0.328	52.6	17.3	14.6	0.847	3.00	0.00
Run 5B	1.5	0.334	51.3	17.1	14.5	0.847	0.70	0.00
Run 5C	2.8	0.337	51.2	17.3	14.5	0.838	0.00	0.00
2 mm olive pit-based								
Uncoated								
	--	0.355	41.4	14.7	12.4	0.847	5.7	0.22
Coated								
Run 6A	0.7	0.347	44.2	15.4	12.3	0.801	1.24	0.04
Run 6B	1.4	0.353	44.2	15.6	12.3	0.789	0.23	0.01
Run 6C	2.4	0.356	43.5	15.5	12.2	0.791	1.60	0.00

* Same sample, duplicate measurements--to obtain representative average reading.

[0041] Compared with their respective uncoated base carbons, initial dust and dust rate are sharply reduced. Butane working capacity and butane activity, on a volume basis, are unaffected.

Example 4

[0042] Acrylic copolymer is another example of an active carbon coating material, in addition to the previously cited polyethylene and silicone materials, in the present invention. BAX 1100 and BAX 1500 active carbon pellets were coated in the lab with JONREZ® E-2062, an acrylic copolymer salt solution produced by Westvaco Corporation.

[0043] The coatings were applied by the previously described method of Example 1. After evaluating the properties of two samples of uncoated BAX 1500, two samples of the same BAX 1500 plant production were coated with a 9.0 wt% solids acrylic copolymer emulsion. Similarly, after measuring the properties of a sample of uncoated BAX 1100, a sample of the same BAX 1100 plant production was coated with a 6.0 wt% solids acrylic copolymer emulsion. A dedusting step was not applied prior to analyzing the coated products. The coating loading on BAX 1500 was determined by heating samples to 932°F (500°C) and measuring the amount of volatilized components with a hydrocarbon analyzer calibrated with carbons of known acrylic copolymer content. The coating loading on BAX 1100 was derived from the wet-basis weight gain of the coated sample and the amount of applied emulsion spray. The acrylic copolymer coating has the same benefits as previously shown with polyethylene and silicone for reducing dust without significant effect on key properties, as shown in Table IV.

Table IV

Sample IP	Coating (wt%)	AC (g/mL)	Butane Activity (%)	Butane Activity (g/dL)	BWC (g/dL)	Butane Ratio	Initial Dust (mg/dL)	Dust Rate (mg/min/dL)
Uncoated								
BAX 1500 ¹								
	--	0.282	66.5	18.8	16.2	0.865	2.24	0.15
	--	0.283	62.9	17.8	15.8	0.890	3.31	0.11
average:		0.283	64.7	18.3	16.0	0.878	2.78	0.13
Coated with Acrylic								
Copolymer								
Run 7A	1.6 ²	0.277	65.0	18.0	15.6	0.868	1.93	0.01
Run 7B	3.4 ³	0.283	64.7	18.3	15.8	0.862	1.30	0.00
Uncoated								
BAX 1100 ³								
	-	0.361	35.0	12.6	10.9	0.864		
	-	<u>0.353</u>	<u>35.0</u>	<u>12.4</u>	<u>10.9</u>	<u>0.883</u>	<u>11.40</u>	<u>0.69</u>
average:		0.357	35.0	12.5	10.9	0.874	11.40	0.69
Coated with Acrylic								
Copolymer								
Run 8	4.3 ⁴	0.352	34.0	12.0	10.2	0.856	1.02	0.00

¹ Noted as Uncoated wood-based samples in Table III

² Measured by hydrocarbon analyzer method

³ Noted as "Uncoated" sample in Table I

⁴ Average of 1.0 and 7.7 wt% (from wet-basis weight gain and emulsion solids sprayed, respectively)

[0044] The data show that a 1.6 wt% polymer coating on the BAX 1500 shaped active carbon essentially eliminated dusting, with only an insignificant loss in BWC. Even more surprising is that a 3.4 wt% coating on the same active carbon material achieved total elimination of dusting, with a negligible loss in BWC. Also, a 4.3 wt% coating of the BAX 1100 shaped active carbon achieved a total elimination of dusting, with only a 6.4% reduction of BWC.

[0045] Thus, the subject matter of the applicants' invention is:

(1) A composition of matter comprising an activated carbon material exhibiting initial, pre-coating butane activity and butane working capacity values and having its surface coated with a continuous film of a polymer, said polymer film being operable for essentially eliminating attrition of the activated carbon material resulting from dusting and wherein the coated activated carbon material exhibits final, post-coating butane activity and butane working capacity values at least 90% of the initial, pre-coating butane activity and butane working capacity values, respectively;

(2) a process for essentially eliminating dust attrition of activated carbon material exhibiting initial, pre-coated butane activity and butane working capacity values comprising the step of coating the activated carbon material surface with a continuous film of a polymer wherein the coated activated carbon material exhibits final, post-coating butane activity and butane working capacity values at least 90% of the initial, pre-coating butane activity and butane working capacity values, respectively;

(3) a process for essentially eliminating dust attrition of activated carbon material by coating the activated carbon material comprising the steps of:

(a) spraying an emulsion of the polymer onto exposed surfaces of the activated carbon material while it is in a state of turbulence at a processing temperature above ambient temperature; and

(b) drying the coated activated carbon material at above ambient temperature; and

(4) a composition of matter comprising an activated carbon material having its surface coated with a continuous film of a polymer, said polymer film being operable for essentially eliminating attrition of the activated carbon material resulting from dusting and the coated activated carbon exhibiting a butane activity value greater than 15 g/100g.

[0046] While the preferred embodiments of the present invention have been described, it should be understood that various changes, adaptations, and modifications may be made thereto without departing from the spirit of the invention and the scope of the appended claims. It should be understood, therefore, that the invention is not to be limited to minor details of the illustrated invention shown in preferred embodiment and the figures and that variations in such minor details will be apparent to one skilled in the art. The claims, therefore, are to be accorded a range of equivalents commensurate in scope with the advances made over the art.

Claims

1. A composition of matter comprising an activated carbon material exhibiting initial, pre-coating butane activity and butane working capacity values and having its surface coated with a continuous film of a polymer, said polymer film being operable for essentially eliminating attrition of the activated carbon material resulting from dusting and wherein the coated activated carbon material exhibits final, post-coating butane activity and butane working capacity values at least 90% of the initial, pre-coating butane activity and butane working capacity values, respectively.
2. The composition of claim 1 wherein the final, post-coating butane activity and butane working capacity values are at least 95% of the initial, pre-coating butane activity and butane working capacity values, respectively.
3. The composition of claim 1 wherein the final, post-coating butane activity and butane working capacity values are at least 98% of the initial, pre-coating butane activity and butane working capacity values, respectively.
4. The composition of claim 1 wherein the final, post-coating butane activity and butane working capacity values are at least 100% of the initial, pre-coating butane activity and butane working capacity values, respectively.
5. A process for essentially eliminating dust attrition of activated carbon material exhibiting initial, pre-coated butane activity and butane working capacity values comprising the step of coating the activated carbon material surface with a continuous film of a polymer wherein the coated activated carbon material exhibits final, post-coating butane activity and butane working capacity values at least 90% of the initial, pre-coating butane activity and butane working capacity values, respectively.
6. The process of claim 5 wherein the final, post-coating butane activity and butane working capacity values are at least 95% of the initial, pre-coating butane activity and butane working capacity values, respectively.
7. The process of claim 6 wherein the final, post-coating butane activity and butane working capacity values are at least 98% of the initial, pre-coating butane activity and butane working capacity values, respectively.
8. The process of claim 7 wherein the final, post-coating butane activity and butane working capacity values are at least 100% of the initial, pre-coating butane activity and butane working capacity values, respectively.
9. A process for essentially eliminating dust attrition of activated carbon material by coating the activated carbon material comprising the steps of:
 - (a) spraying an emulsion of the polymer onto exposed surfaces of the activated carbon material while it is in a state of turbulence at a processing temperature above ambient temperature; and
 - (b) drying the coated activated carbon material at above ambient temperature.
10. The process of claim 9 comprising a further step

(c) de-dusting the dry coated activated carbon material by removing any residual dust therefrom.

11. The process of claim 9 further comprising an initial step of heating the active carbon material at above ambient temperature.

12. The process of claim 9 wherein the processing temperature is maintained from above ambient to 280°F (138°C) for from about 1 minute to about 12 hours.

13. The process of claim 12 wherein the processing temperature is maintained from about 100°F (38°C) to about 250°F (121°C) for from about 5 minutes to about 6 hours.

14. The composition of claim 1 wherein the polymer is selected from the group consisting of polyethylene, polypropylene, polyisobutylene, polystyrene, polyisoprene, polychloroprene, poly-4-methyl-1-pentene, polybutadiene, polybutene, polyacrylate, polymethyl methacrylate, polybutylmethacrylate, polymethacrylates, polyacrylic acid, polytetrafluoroethylene, trifluoroethylene, vinyl fluoride, fluorovinylidene, fluorobutylene, fluoropropylene, polyurethane, polyethylene terephthalate, styrene butadiene, modified polybutadiene, epoxies, modified alkyds, polyesters, starches, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, polyvinyl acetate, cellulose acetate, cellulose nitrate, cellulose triacetate, cellulose acetate, phthalate, cellulose propionate morpholinobutyrate, hydroxypropylmethyl cellulose, ethylene vinyl acetate, acrylic polymers and copolymers, polysulfones, polyether sulfones, polyethers, polyethylene, glycols, polyimines, polybutylene, polyvinyl ethers, polyvinyl esters, polyalkylsulfides, polyarylsulfides, lignosulfonates, polyacrylamide, cyanoacrylate, polyamides, polyimides, polysiloxanes, methacrylonitrile, polyacrylonitrile, polyvinyl pyridine, polyvinyl benzene, polyvinyl acetate, polyvinyl pyrrolidene, polyvinyl butyral, polyvinyl alcohol, polyvinyl chloride, polyvinyl formaldehyde, polyformaldehyde, polycarbonates, and polyvinylidene chloride.

15. The composition of claim 14 wherein the polymer is selected from the group consisting of acrylic polymer and polyethylene.

16. The composition of claim 1 wherein the active carbon material is derived from a member of the group consisting of coal, lignocellulosic materials, petroleum, bone, and blood.

17. The composition of claim 16 wherein the lignocellulosic materials are selected from the group consisting of including pulp, paper, residues from pulp production, wood chips, sawdust, wood flour, nut shell, kernel, and fruit pits.

18. The process of claim 5 wherein the polymer is selected from the group consisting of polyethylene, polypropylene, polyisobutylene, polystyrene, polyisoprene, polychloroprene, poly-4-methyl-1-pentene, polybutadiene, polybutene, polyacrylate, polymethyl methacrylate, polybutylmethacrylate, polymethacrylates, polyacrylic acid, polytetrafluoroethylene, trifluoroethylene, vinyl fluoride, fluorovinylidene, fluorobutylene, fluoropropylene, polyurethane, polyethylene terephthalate, styrene butadiene, modified polybutadiene, epoxies, modified alkyds, polyesters, starches, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, polyvinyl acetate, cellulose acetate, cellulose nitrate, cellulose triacetate, cellulose acetate, phthalate, cellulose propionate morpholinobutyrate, hydroxypropylmethyl cellulose, ethylene vinyl acetate, acrylic polymers and copolymers, polysulfones, polyether sulfones, polyethers, polyethylene, glycols, polyimines, polybutylene, polyvinyl ethers, polyvinyl esters, polyalkylsulfides, polyarylsulfides, lignosulfonates, polyacrylamide, cyanoacrylate, polyamides, polyimides, polysiloxanes, methacrylonitrile, polyacrylonitrile, polyvinyl pyridine, polyvinyl benzene, polyvinyl acetate, polyvinyl pyrrolidene, polyvinyl butyral, polyvinyl alcohol, polyvinyl chloride, polyvinyl formaldehyde, polyformaldehyde, polycarbonates, and polyvinylidene chloride.

19. The process of claim 18 wherein the polymer is selected from the group consisting of polysiloxane, acrylic copolymer and polyethylene.

20. The composition of claim 1 wherein the active carbon material is derived from a member of the group consisting of coal, lignocellulosic materials, petroleum, bone, and blood.

21. The composition of claim 20 wherein the lignocellulosic materials are selected from the group consisting of including pulp, paper, residues from pulp production, wood chips, sawdust, wood flour, nut shell, kernel, and fruit pits.

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22. A composition of matter comprising an activated carbon material having its surface coated with a continuous film of a polymer, said polymer film being operable for essentially eliminating attrition of the activated carbon material resulting from dusting and the coated activated carbon exhibiting a butane activity value greater than 15 g/100g.

5 23. The composition of claim 22 wherein the coated activated carbon exhibits a butane activity value greater than 25 g/100g.

24. The composition of claim 23 wherein the coated activated carbon exhibits a butane activity value greater than 35 g/100g.

10 25. The composition of claim 24 wherein the coated activated carbon exhibits a butane activity value greater than 45 g/100g.

26. The composition of claim 25 wherein the coated activated carbon exhibits a butane activity value greater than 55 g/100g.

15 27. The composition of claim 26 wherein the coated activated carbon exhibits a butane activity value greater than 65 g/100g.

20 28. The composition of claim 27 wherein the coated activated carbon exhibits a butane activity value greater than 75 g/100g.

29. The composition of claim 22 further comprising a dust rate value no greater than 0.06 mg/min/dL.

25 30. The composition of claim 1 further comprising a dust rate value no greater than 0.06 mg/min/dL.

Figure 1
BWC

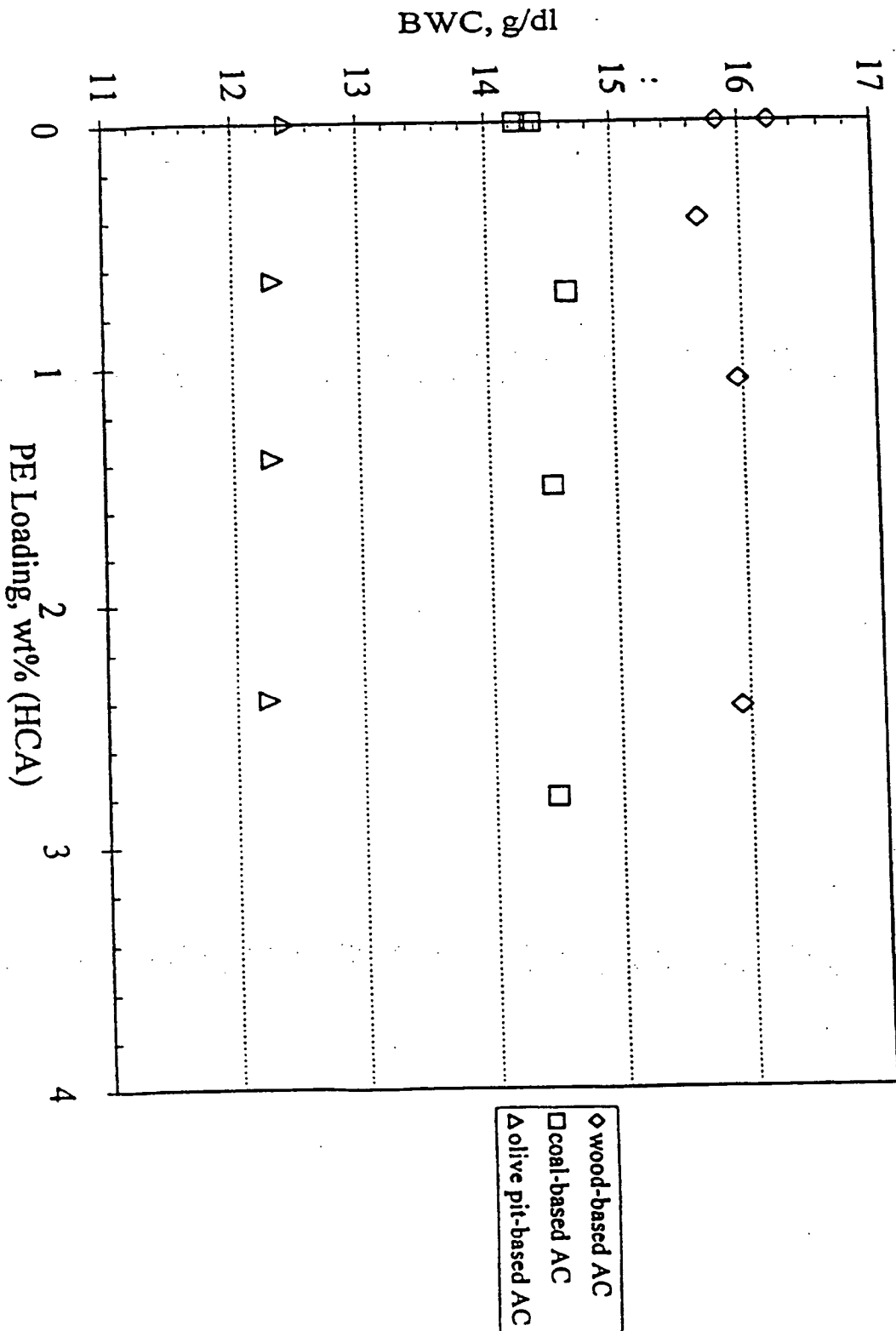


Figure 2
Initial Dust

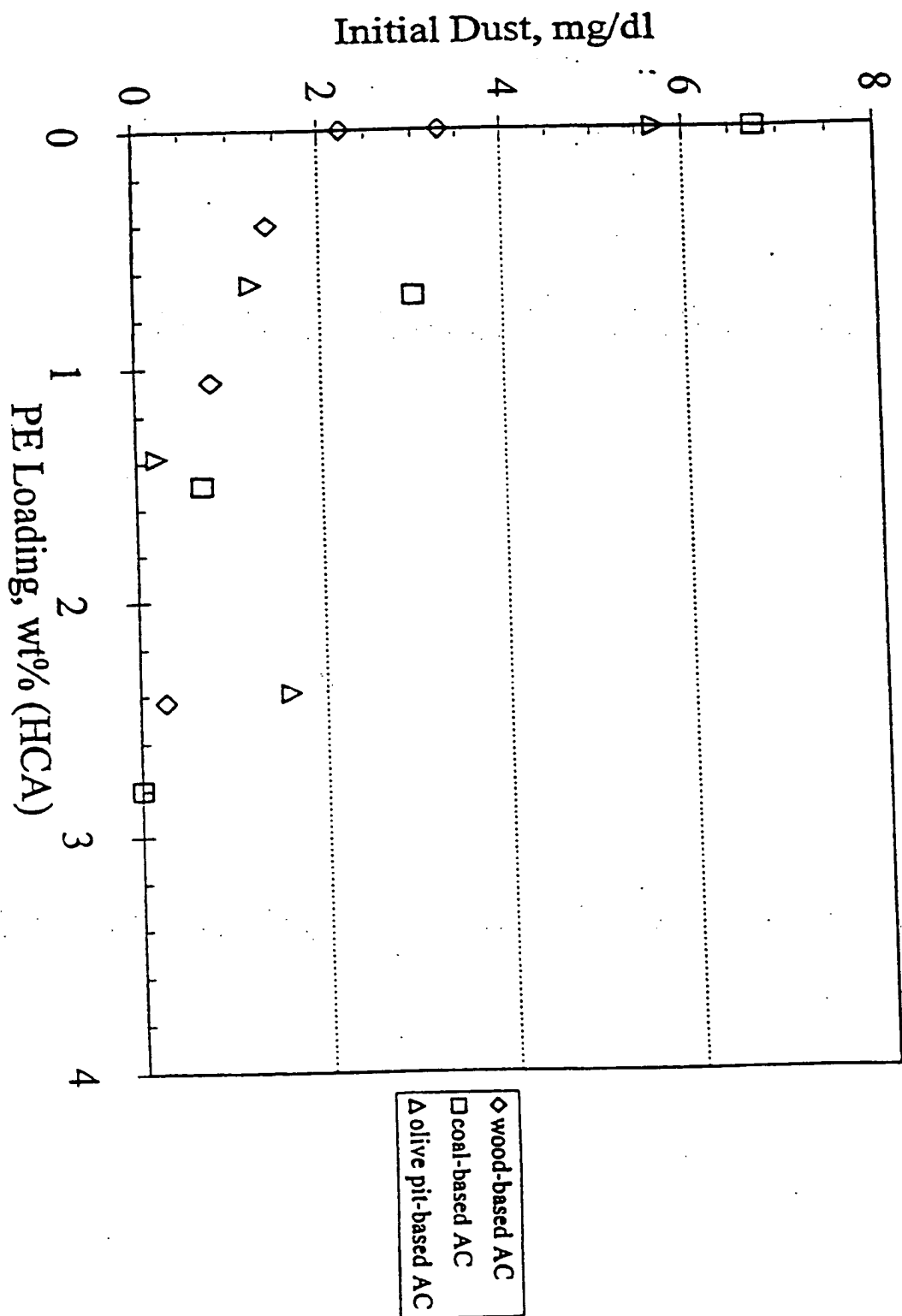
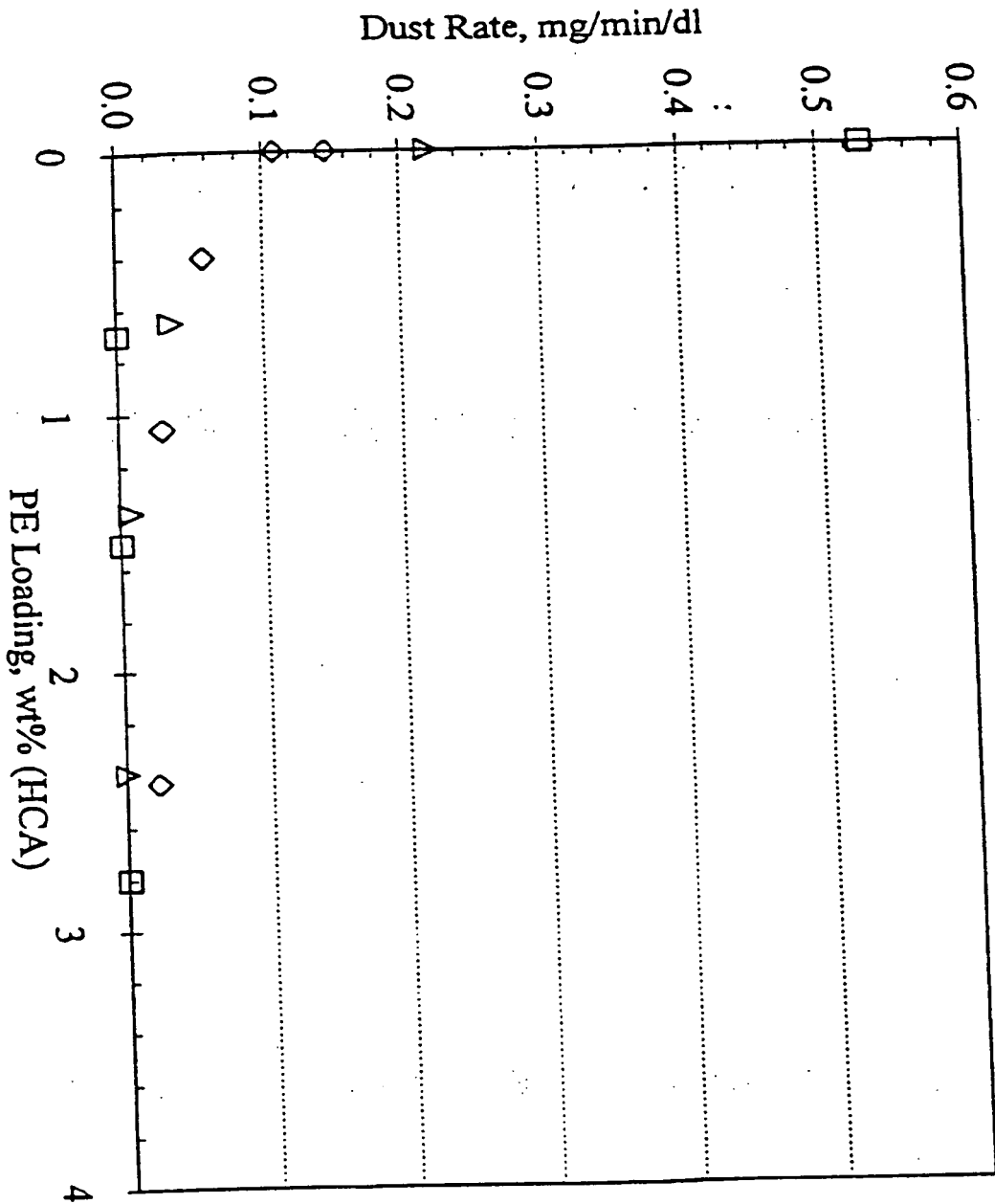


Figure 3
Dust Rate



◇ wood-based AC
□ coal-based AC
△ olive pit-based AC



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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 2722

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DATABASE WPI Section Ch, Week 197423 Derwent Publications Ltd., London, GB; Class A82, AN 1974-42699V XP002161603 & JP 49 018556 B (M KOMIYAMA), 10 May 1974 (1974-05-10) * abstract *	1,5,14, 15,18,19	C01B31/08
X	DATABASE WPI Section Ch, Week 197634 Derwent Publications Ltd., London, GB; Class A97, AN 1976-63877X XP002161604 & JP 50 039692 A (TSURUMI COAL KK), 11 April 1975 (1975-04-11) * abstract *	1,5,14, 15,18, 19,22	
X	EP 0 224 978 A (SHISEIDO CO LTD) 10 June 1987 (1987-06-10) * page 1 * * page 25 * * claims 1-5 *	1,5,18, 19,22	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C01B
X	DATABASE WPI Section Ch, Week 199247 Derwent Publications Ltd., London, GB; Class A17, AN 1992-386190 XP002161605 & JP 04 285006 A (KURARAY CHEM CO LTD), 9 October 1992 (1992-10-09) * abstract *	1,5, 14-17,22	
X	DE 24 13 220 A (TOYO JOZO KK) 26 September 1974 (1974-09-26) * the whole document *	1,5,14, 15,18, 19,22	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 February 2001	Examiner Puetz, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 2722

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DE 29 46 645 A (VNI ISPYTATELNY INST MED TEKH) 27 May 1981 (1981-05-27) * claims; examples *	1,5,14, 18	
X	EP 0 090 306 A (BASF AG) 5 October 1983 (1983-10-05) * the whole document *	1,5,14, 15,18, 19,22	
X	DE 38 01 457 A (BLUECHER HASSO VON ;RUITER ERNEST DE (DE)) 3 August 1989 (1989-08-03) * the whole document *	1,5,14, 18,22	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 February 2001	Examiner Puetz, C
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EP/FORM 1503 03/82 (FodC01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 10 2722

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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28-02-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 49018556 B	10-05-1974	NONE	
JP 50039692 A	11-04-1975	NONE	
EP 0224978 A	10-06-1987	CA 1294835 A	28-01-1992
		CA 1261208 A	26-09-1989
		DE 3650660 D	15-01-1998
		DE 3650660 T	07-05-1998
		DE 3683605 A	05-03-1992
		DE 3684836 A	21-05-1992
		EP 0212870 A	04-03-1987
		EP 0417866 A	20-03-1991
		US 4882225 A	21-11-1989
		US 4801445 A	31-01-1989
		US 4818614 A	04-04-1989
		JP 1054380 B	17-11-1989
		JP 1635593 C	20-01-1992
		JP 63113081 A	18-05-1988
		JP 1054381 B	17-11-1989
		JP 1974244 C	27-09-1995
		JP 63113082 A	18-05-1988
JP 4285006 A	09-10-1992	NONE	
DE 2413220 A	26-09-1974	JP 921049 C	05-09-1978
		JP 49117401 A	09-11-1974
		JP 53000752 B	11-01-1978
		CA 1019309 A	18-10-1977
		CH 593087 A	30-11-1977
		FR 2222129 A	18-10-1974
		GB 1462088 A	19-01-1977
		SE 423597 B	17-05-1982
		US 3953360 A	27-04-1976
DE 2946645 A	27-05-1981	NONE	
EP 0090306 A	05-10-1983	DE 3211629 A	06-10-1983
		DE 3360707 D	10-10-1985
		JP 58177141 A	17-10-1983
		US 4535005 A	13-08-1985
DE 3801457 A	03-08-1989	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82